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RDX Transformation In Biotic and Abiotic Systems Under Poised Redox Potentials

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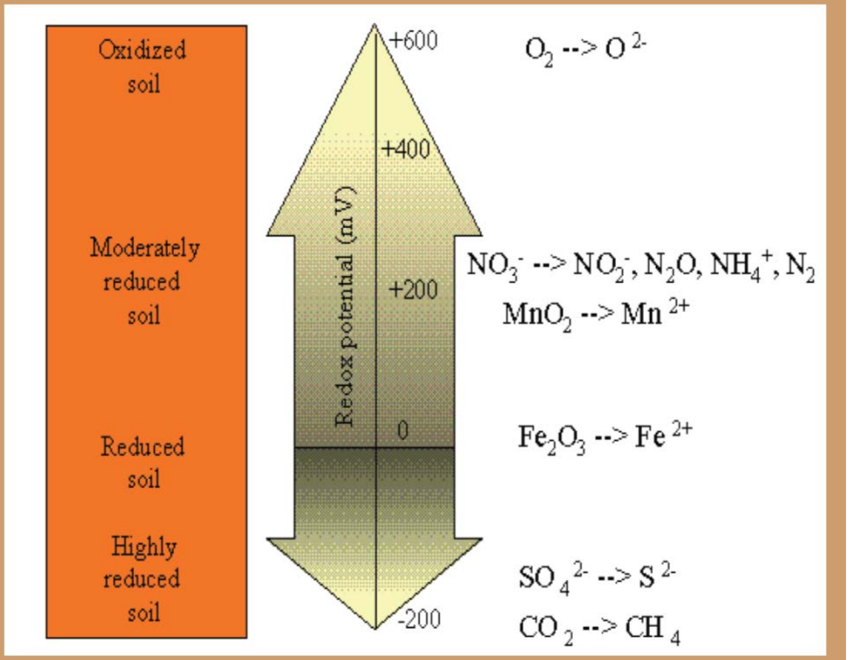
Background

- Hexahydro-1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX) is present in soils due to training and other activities
- *In situ* techniques exist to degrade RDX
- RDX degradation could be enhanced if biogeochemical factors could be determined and/or controlled.
- Purpose was to determine the role redox potentials play in RDX degradation.



Redox potentials for common environmental electron accepting processes

Hypothesis

Biological processes of nitrate, iron, and sulfate-reducing bacteria create conditions conducive not only to direct enzymatic RDX transformations, but also to indirect abiotic RDX degradation.

Approach–3 test systems

1. **Biological**: Mixed consortium amended with terminal electron acceptor and RDX. Controls did not contain inoculum.
2. **Biologically poised (abiotic**): Biological cultures with terminal electron acceptor were grown until Eh was reduced (30 days). Cultures were autoclaved and amended with RDX. Controls did not contain inoculum.
3. **Chemically poised**: RDX solutions containing terminal electron acceptor. Eh of solutions were chemically reduced. RDX in a buffer solution was control.

Approach–continued

Mixed Culture:

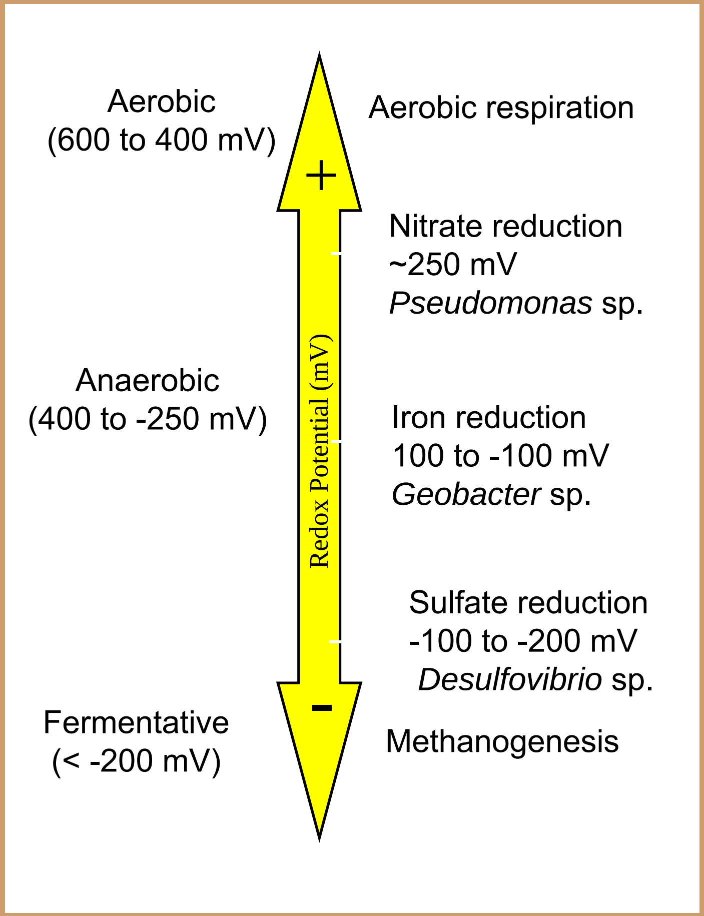
- *Pseudomonas aeruginosa* – nitrate reducer
- *Geobacter metallireducens* GS-15 – iron reducer
- *Desulfovibrio desulfuricans* G20 – sulfate reducer

Nutrient broth:

- Electron acceptor: Fe^{3+}, NO_3^-, or SO_4^{3-} at 10 mM
- RDX at 1 or 4 ppm (5 and 20 µM)
- Buffered to maintain pH 7.
- Initial ORP= 300mV
- N-Tris(hydroxymethyl)methyl-2-aminoethanesulfonic acid
  - Buffer for Biotic cultures
- tris(hydroxymethyl) aminomethane
  - Buffer for chemically poised systems

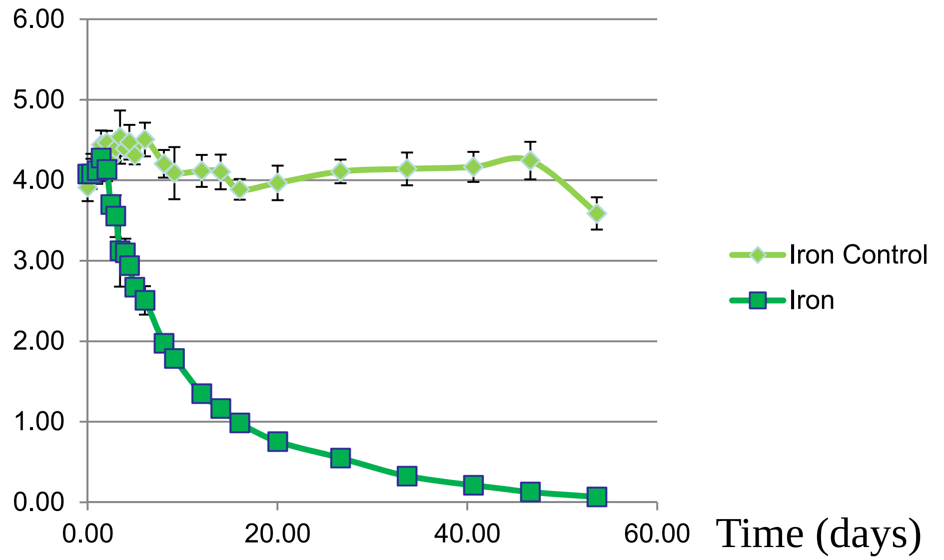
Analysis

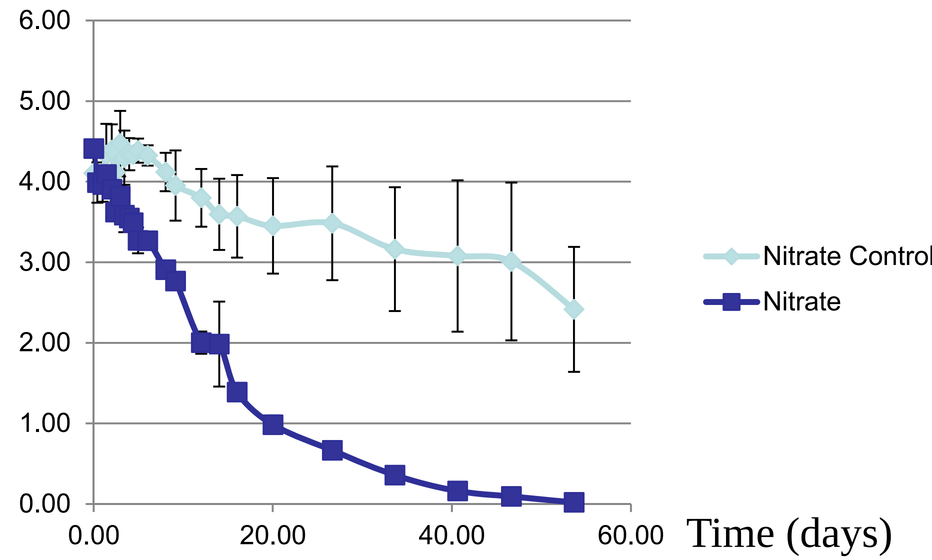
- Explosives (HPLC)
- pH: pH electrode
- Eh: Pt electrode and Ag Cl reference
- Amendments: IC
- Organic transformation products (HPLC-ESI-MS)

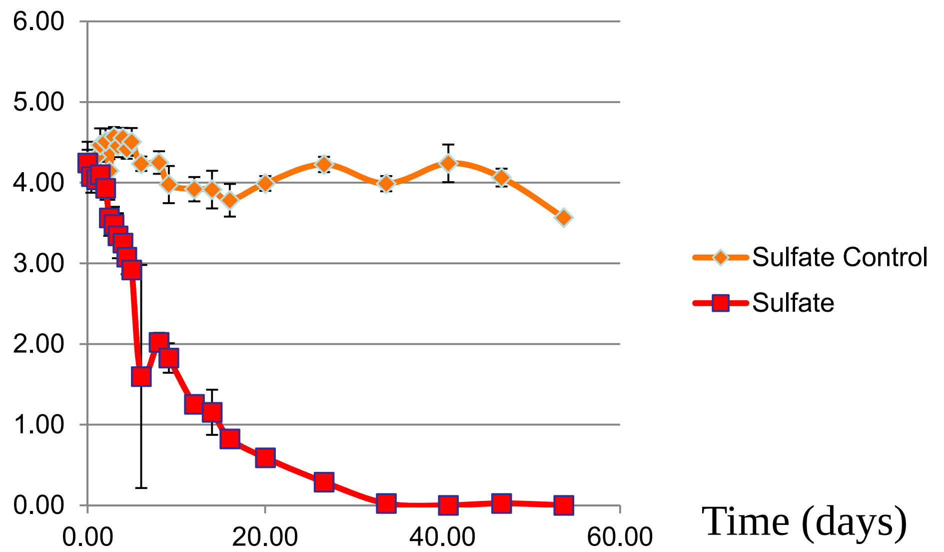


Biological RDX reduction

RDX concentration (ppm) versus time (days)

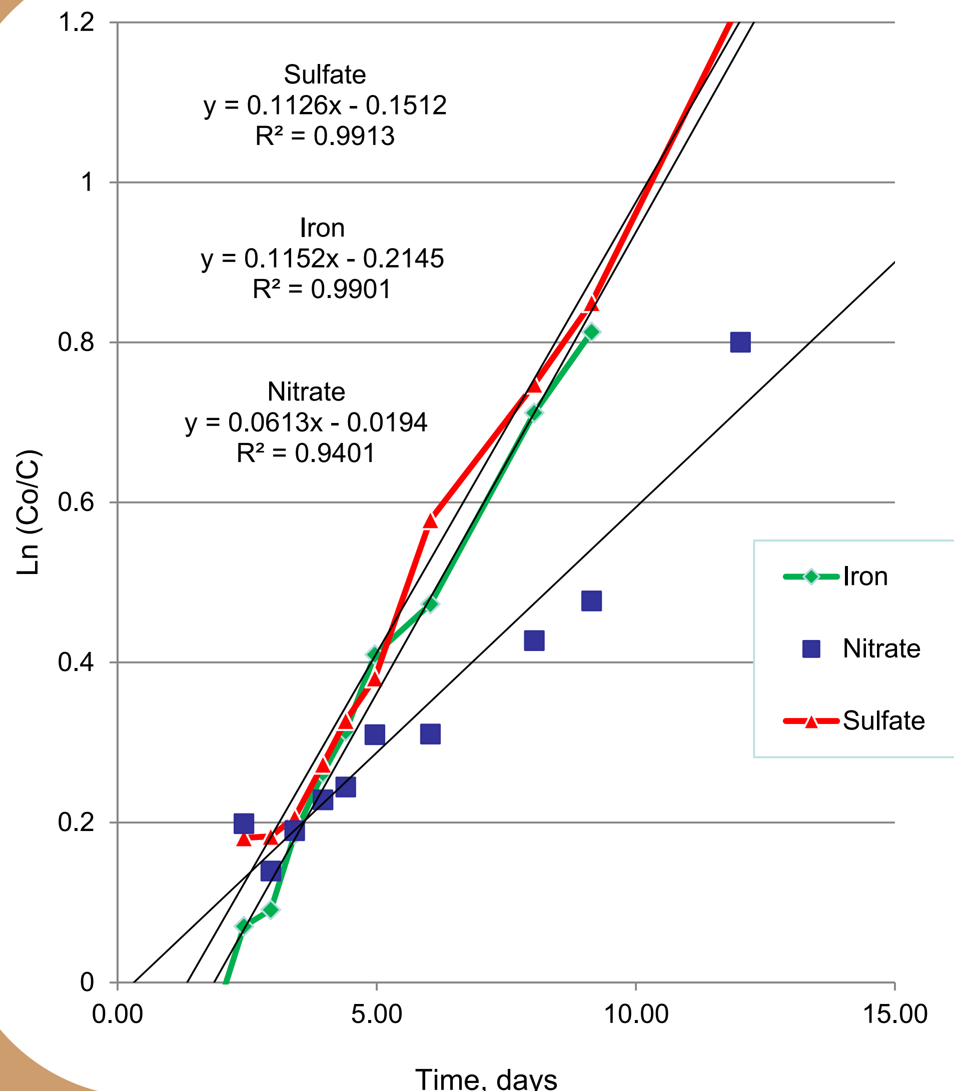






RDX was degraded under all three conditions in the biological systems.

Kinetics of biological RDX reduction



For first-order rate kinetics analysis: $C=C_0e^{-kt}$
in which: C= concentration mg/L
k=reaction rate per day
t= time in days

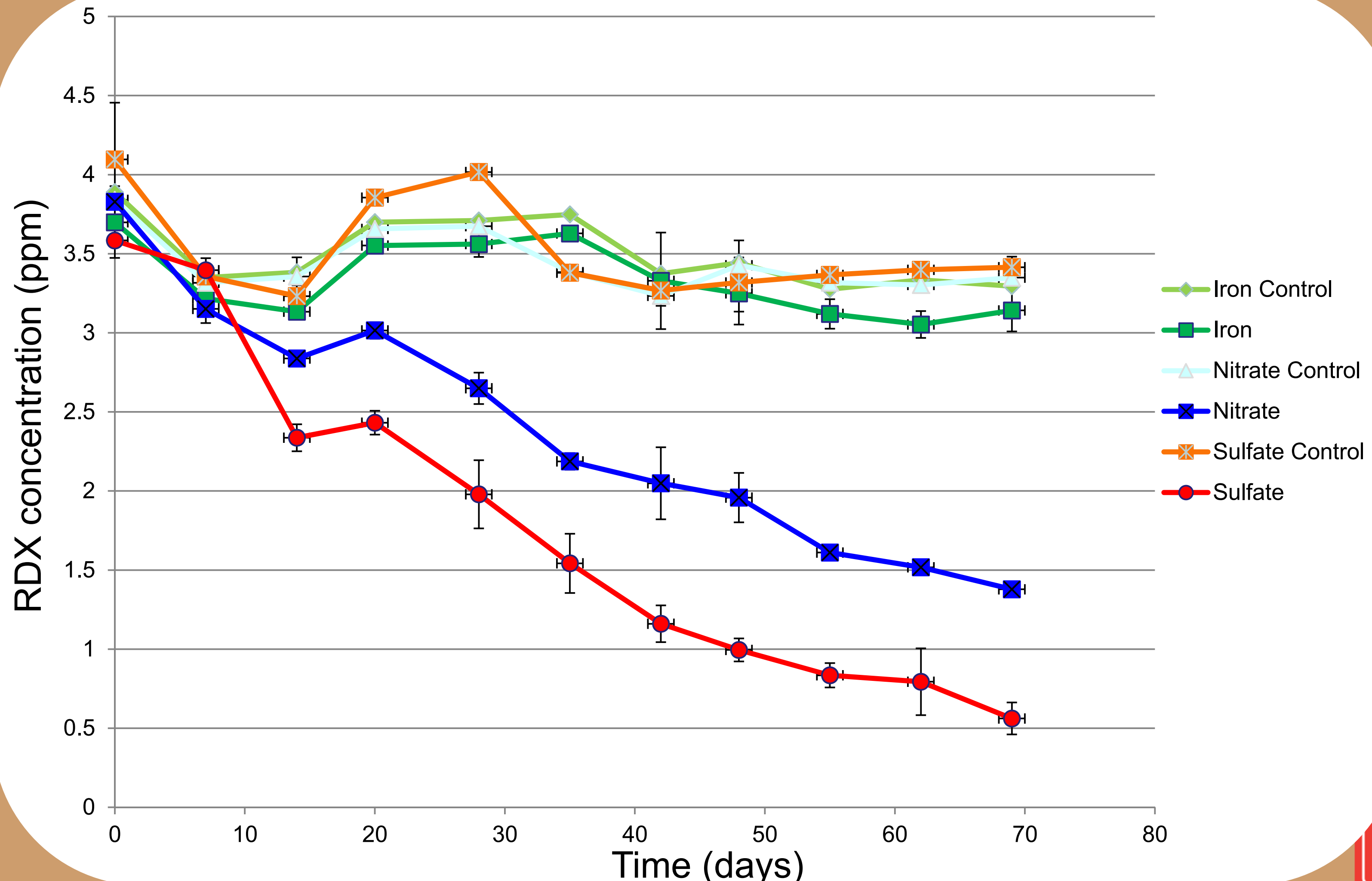
Linearization yields
$\ln (C_0/C)=kt$

	Iron	Sulfate	Nitrate
k, per day	0.1152	0.1126	0.0613
Half life, days	6.01	6.15	11.31

First Order Rate Kinetics

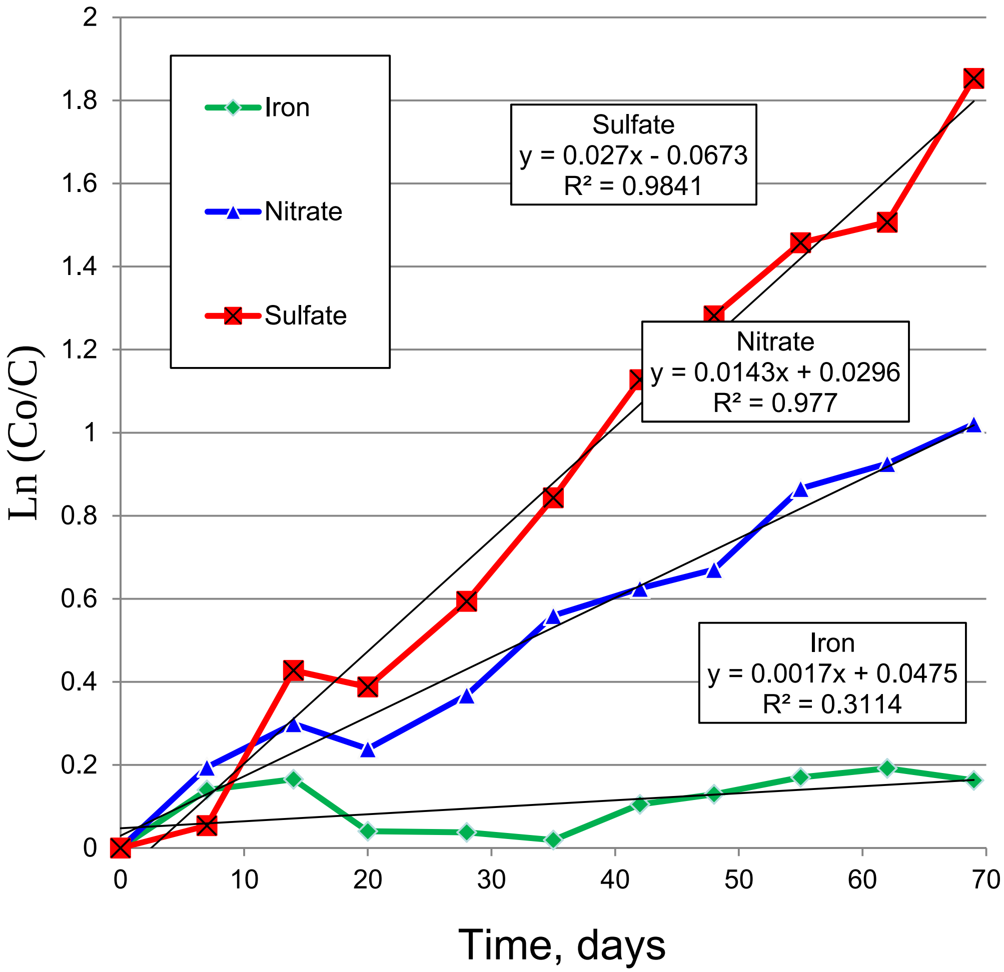
Abiotic RDX reduction

Eh was reduced by biological activity, autoclaved, and amended.



Kinetics of abiotic RDX reduction

Biotic degradation was much faster—rates are at least 4X abiotic rates



For first-order rate kinetics analysis: $C=C_0e^{-kt}$

in which:

C= concentration in mg/L

k =reaction rate per day

t = time in days

First Order Rate Kinetics

	Iron	Sulfate	Nitrate
k, per day	.0017	.027	.0143
Half life, days	407.7	25.7	48.5
Half life, biological reduction	6.01	6.15	11.31

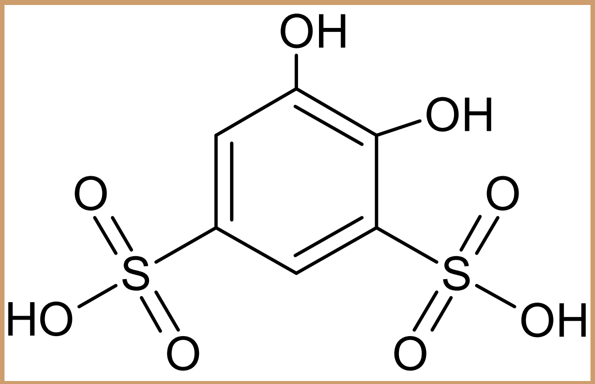
Chemically poised systems

- Iron (II) as the reductant
- Sulfur/Sulfide as the reductant
- Nitrogen compounds as the reductant

Iron System

- Used 2 mM Iron (II) solutions in Tris Buffer with a Tiron ligand at pH 7.5-8
  - ► Ferrous Sulfate – Fe(II)
  - ► Ferric Sulfate – Fe(III)

Iron-facilitated abiotic degradation of RDX only occurs under anaerobic conditions.



Tiron

Iron System

Iron Species	pH	Eh	RDX Degradation
Single Iron Solutions			
Fe (II)	7.58	-240	Yes
Fe (II)	7.62	-268	Yes
Fe (II)	7.71	-201	Yes
Fe(III)	7.61	-220	No*
Mixed Iron Solutions (50: 50):			
Fe(II):Fe(III)	7.72	-223	Yes
Fe(II):Fe(III)	7.68	-255	Yes

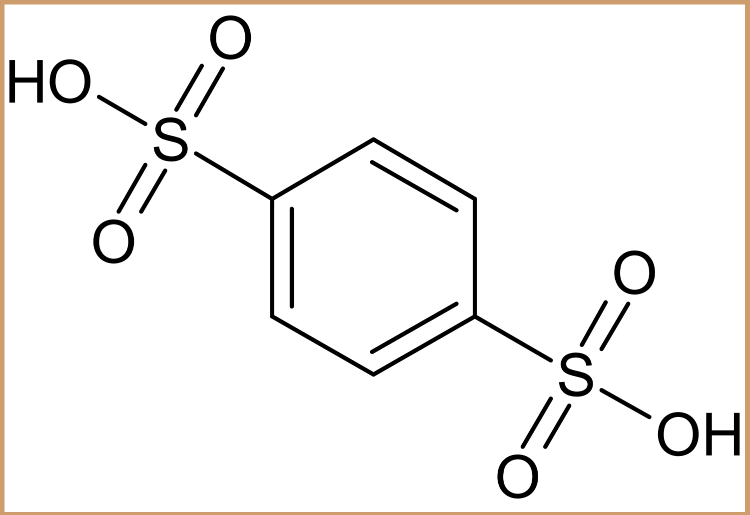
- Iron (II) was a successful reductant for RDX
- Iron (III) exhibited minimal potential for RDX degradation

Iron facilitated RDX degradation is most likely to occur in reducing environments (< -150 mV)

Sulfur/Sulfide Systems

The effectiveness of Sulfur/Sulfide as a reductant were evaluated using:

- H_2S bubbled Tris buffer solution
- Elemental Sulfur
- Dithiolbenzene (DBT)
- Sodium Sulfate
- Sodium Sulfide



dithiolbenzene

Sulfur/Sulfide Systems

DBT Experiment	pH	Eh	RDX Degradation
DBT alone			
	8.3	-136	Yes
	8.5	-92	Partial
DBT + Iron			
	8.5	-477	Yes
	8.5	-380	Yes
	9	-467	Yes
	9	-403	Yes

- Dithiolbenze is effective at abiotically degrading RDX
- It is highly effective in the presence of Iron (II)

Nitrogen Systems

The effectiveness of Nitrogen as a reductant was evaluated using:

- 1.5 mM Hydroxylamine
  - ► pH/Eh: 3.9/-180; 6.0/-195; 8.0/-256
- 1 mM Sodium Nitrite
  - ► pH/Eh: 8.0/-238
- 1 mM Sodium Nitrate
  - ► pH/Eh: 5.0/-246; 7.1/-261; 8.0/-266

RDX did not degrade in the presence of these N- compounds

Summary of Chemically Poised tests

- We found iron to be effective at very low Eh values and under anaerobic conditions.
- Sulfur can also be an effective reductant (depending on its form). Sulfides cause degradation, while sulfates and elemental sulfur does not.
- The nitrogen compounds used did not cause RDX degradation under these experimental parameters.

Eh – pH Comparison

	Iron	Sulfate	Nitrate
Biological Eh	-63mV	-154 mV	-237 mV
pH	7	7	7
Abiotic Eh	-30 mV *	-230 mV	-215 mV
pH	7-8	7-8	7-8
Chemically Poised Eh	< -150 mV	-150 mV (DTB) -400 mV (DTB-Fe)	-60 mV *
pH	7.5 - 8	6 – 8.5	6 -8

* Indicates that RDX did not degrade in this system

Conclusions

- **Original hypothesis:** Biological processes of nitrate, iron, and sulfate-reducing bacteria create conditions conducive not only to direct enzymatic RDX transformations, but also to indirect abiotic RDX degradation.
- Abiotic degradation takes place under nitrate and sulfate reducing conditions that were initiated by a bacterial consortium. Abiotic iron systems did not efficiently degrade RDX.
- Abiotic degradation is much slower than biological degradation.
- RDX degraded in systems that were at neutral pH and generally at Eh values < -150 mV. Fe biological system was exception.

Project Team

- ►Dr. Heather Smith – ERDC-EL
- ►Dr. Jennifer Seiter – ERDC-EL
- ►Dr. Anthony Bednar – ERDC-EL
- ►Mr. Clint Arnett – ERDC-CERL
- ►Deborah Ragan – Badger Technical Services

Thanks for your attention!

Sulfur/Sulfide Systems

- Results show that elemental sulfur alone did not result in degradation of RDX at neutral pHs.
  - pH/Eh: 7.0/-280; 8.0/-285

- 10 mM Sodium Sulfate did not cause RDX degradation
  - pH/Eh: 4.8/-258; 7.1/-270; 8.0/-275

- 100 mM Sodium Sulfide effectively degraded RDX at a pH of 12, and partially degraded it at pHs 8 and 10.
  - pH/Eh: 8.0/-351; 9.9/-355; 12/-361

Lessons Learned

- ► RDX can degrade abiotically under anaerobic conditions that were mediated by biological processes
- ► Abiotic rates are slower than biological rates
- ► Abiotic RDX degradation rates follow sequence

$$SO_4^{-2} > NO_3^{-} > Fe^{+2}$$

- ► Eh values in effective systems were usually <-150 mV, in neutral solutions. Fe biological system was unique.
- ► RDX was not degraded until after nitrate was depleted – Eh value is not low enough.